# Dearomatization of Naphthalene: Stereoselective *cis*-1,4 Tandem Additions Promoted by Osmium(II)

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**Abstract:** The naphthalene complex of pentaammineosmium(II) (**1**) reacts with four different classes of electrophiles to form 1-naphthalenium species **2**−**5**. These $\eta^3$-allyl complexes react stereospecifically with a variety of nucleophiles to form *cis*-1,4-dihydronaphthalene complexes. The entire reaction sequence may be performed outside a glovebox in two steps using conventional techniques.

## Introduction

Given the abundance of compounds in nature that contain dihydronaphthalene or tetralin cores, efficient methods for the preparation of these materials are highly desirable.[1−3] Procedures that generate functionalized dihydronaphthalenes directly from their aromatic precursors have become valuable tools to the synthetic chemist, due to the availability and stability of naphthalene and substituted naphthalenes. For many years, the Birch reduction has been the primary synthetic method to achieve this transformation,[4] yet this reaction has limitations. Only hydrogen and unfunctionalized alkyl groups can be introduced during the dearomatization, and the reaction conditions are incompatible with many functional groups. Regioselectivity is often poor, and over-reduction is a common problem. Although recent modifications of the Birch reduction such as the use of silylated naphthalenes expand its utility,[5,6] regio- and stereocontrol can still be problematic.

Our interest in the ability of pentaammineosmium(II) to activate aromatic systems toward electrophilic additions[7] led us to consider the possibility of generating dihydronaphthalenes by a pathway involving a sequential addition of an electrophile and a nucleophile. The naphthalene complex $[Os(NH_3)_5(\eta^2$-naphthalene$)](OTf)_2$ (**1**) is readily protonated with triflic acid (HOTf) in acetonitrile ($CH_3CN$), and the acidity of the resulting 1-naphthalenium species ($pK_a = -8.2$) is considerably weaker than that of the organic naphthalenium ion.[8] We now report that the introduction of carbon-based electrophiles generates a series of naphthalenium complexes that react with nonbasic nucleophiles to generate stable dihydronaphthalene complexes from which the modified organic ligands can be extracted.

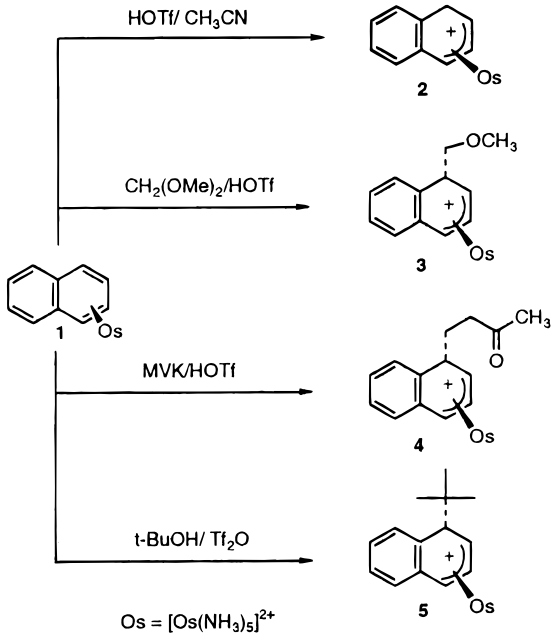


**Figure 1.** Electrophilic addition reactions of $[Os(NH_3)_5(\eta^2$-naphthalene$)](OTf)_2$ (**1**).

## Results

The naphthalene complex of pentaammineosmium(II) (**1**) reacts with triflic acid (HOTf) to generate a solution-stable allyl species, **2** (Figure 1). At ambient temperatures this species slowly decomposes, liberating free naphthalene in the process, but at −40 °C in $CH_3CN$ **2** is stable for days.[8] Although complex **2** is considerably less acidic than its organic counterpart, we found that most nucleophiles reacted as bases with **2** to regenerate compound **1** quantitatively. However, the weak hydride donor triethylsilane reacted with a solution of naphthalenium **2** at 20 °C to form the dihydronaphthalene complex **2a** in a 93% yield (Figure 2). The organic ligand was decomplexed using silver triflate (AgOTf) under mildly basic conditions to yield 1,4-dihydronaphthalene (**2a′**) in 60% yield, 56% overall from naphthalene (Figure 2). 1-Methoxy-2-methyl-1-(trimethylsiloxy)propene (MMTP) also underwent clean addition to C4 with the 1-naphthalenium complex **2** at −40 °C. The product, **2b**, was then oxidized with AgOTf in a $H_2O/CH_3CN$/ether solution, and the organic product was isolated.

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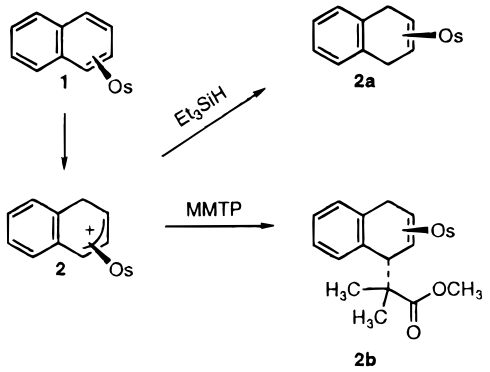


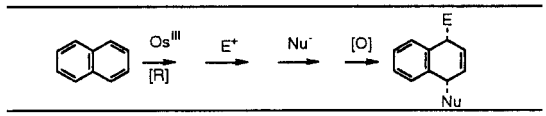

**Figure 2.** Protonation followed by nucleophilic addition to form 1,4-dihydronaphthalene complexes.

Repeating these steps without isolation of complex **2b** or purification of any intermediate resulted in an *overall* 77% yield of the dihydronaphthalene **2b′** (purified, isolated).

Three distinct classes of carbon electrophiles were successfully added to the naphthalene complex **1**. The addition of an acetal, dimethoxymethane, was performed at 20 °C in $CH_3CN$ using HOTf to promote the reaction. After precipitation from diethyl ether, the 1-naphthalenium species **3** was isolated in 88% yield as an analytically pure triflate salt (see Figure 1). The $^1H$ and $^{13}C$ NMR spectra of **3** are overall very similar to those of the parent naphthalenium complex **2**. Three carbon signals at 86.3, 82.4, and 76.4 ppm as well as proton signals at 6.41, 6.13, and 5.52 ppm in $CD_3CN$ confirm $\eta^3$ coordination of the ligand.[8] A singlet at 3.30 ppm in the $^1H$ NMR spectrum and a methylene carbon signal at 73.8 ppm in the $^{13}C$ NMR spectrum further support the assignment of **3** as that shown in Figure 1. In the presence of HOTf in $CH_3CN$, the Michael acceptor methyl vinyl ketone (MVK) reacted in a 1,4 fashion with the naphthalene complex **1** to generate the naphthalenium species **4** (see Figure 1; 90% yield). Complex **4** was precipitated as a triflate salt in analytically pure form from diethyl ether. Spectral features of **4** are similar to the naphthalenium **3** but include two methylene carbons at 38.9 and 28.5 ppm in the $^{13}C$ NMR spectrum and a singlet at 2.05 ppm in the $^1H$ spectrum supporting the assignment shown in Figure 1. Tertiary alcohols also react with the naphthalene complex **1** to form a stable 1-naphthalenium species. For example, when a solution of **1** and *tert*-butyl alcohol in $CH_3CN$ was treated with triflic anhydride, the allyl **5** (see Figure 1) formed in 75% yield. $^1H$ and $^{13}C$ NMR spectra revealed three allyl carbons at 88.0, 86.2, and 77.1 ppm, and their corresponding protons appeared at 6.42, 6.20, and 5.77 ppm ($CD_3CN$). In addition, a large singlet at 1.08 ppm (9H) in the $^1H$ NMR spectrum confirmed the presence of a *tert*-butyl group.

The presence of a carbon substituent at C1 anti to the metal (vide infra) greatly increases the range of nucleophiles capable of reacting successfully with the $\eta^3$-1-naphthalenium complexes (Figure 3). The scope of nucleophilic addition was investigated using the methoxymethyl naphthalenium complex **3**. In a typical reaction procedure, complex **3** was dissolved in $CH_3CN$, and the solution was cooled to −40 °C. Once thermally equilibrated, the allyl solution was added to a chilled solution of nucleophile (−40 °C). After allowing enough time for the nucleophile to react, the complexes were precipitated using a diethyl ether/$CH_2Cl_2$ mixture. All of the complexes in Figure 3 were isolated as triflate salts with yields varying greatly as a result of incomplete precipitation. The main $^1H$ and $^{13}C$ NMR spectral features shared by the 1,4-dihydronaphthalene complexes in acetone-$d_6$ were bound olefin protons shifted upfield by at least 1 ppm and carbon signals for the bound olefin between 55.0 and 45.0 ppm.

**Table 1.** Overall Yields for the Tandem Addition to Naphthalene




| Electrophile | Nucleophile | Overall Yield |
|---|---|---|
| H | H | 56% |
| H | $H_3C$, $H_3C$, $OCH_3$, O | 77% |
| $OCH_3$ | $H_3C$, $H_3C$, $OCH_3$, O | 65% |
| $OCH_3$ | O, O, $H_3CO$, $OCH_3$ | 54% |
| $OCH_3$ | $CH_3$, O | 69% |
| $OCH_3$ | H | 45% |
| $OCH_3$ | $CH_3$ | 40% |
| $OCH_3$ | | 40% |
| $CH_3$, O | O, O, $H_3CO$, $OCH_3$ | 41% |
| | O, O, $H_3CO$, $OCH_3$ | 25% |

The difficulties encountered in precipitating many of the dihydronaphthalene complexes (**3a**−**f**) prompted us to bypass the isolation of these intermediate dihydronaphthalene complexes. Instead, nucleophilic addition was immediately followed by oxidative decomplexation, and the organic product was isolated directly. After the addition of the nucleophile, oxidation of the 1,4-dihydronaphthalene complex was accomplished with the addition of AgOTf. The 1,4-dihydronaphthalene complex solution was first warmed to 20 °C and added to a $H_2O$/ether solution, then AgOTf was added. At the end of 0.5 h, the reaction mixture was heated in a sealed tube. The resulting 1,4-dihydronaphthalene products were obtained after chromatography in overall yields typically in the range of 40−75%. The organic compounds reported in Table 1 were highly air-sensitive in their concentrated form and decomposed in periods as brief as 15−20 min. Thus, the products were frozen in a benzene matrix immediately after chromatography. The yields reported in Table 1 represent isolated yields of a single stereoisomer of the dihydronaphthalene, determined for the four-step reaction sequence. These yields reflect an average yield per chemical step of 80−93%.

The naphthalenium complexes **4** and **5** were also reactive with nucleophiles, and a stabilized enolate was used as an example (Figure 4). The reaction conditions required to form **5** were not compatible with the adaptation of a tandem process, thus complex **5** was first isolated as its triflate salt then redissolved in $CH_3CN$, where it was treated with dimethyl malonate and base. The reaction mixture was then treated with AgOTf, and the organic product **5a′** was isolated and purified.

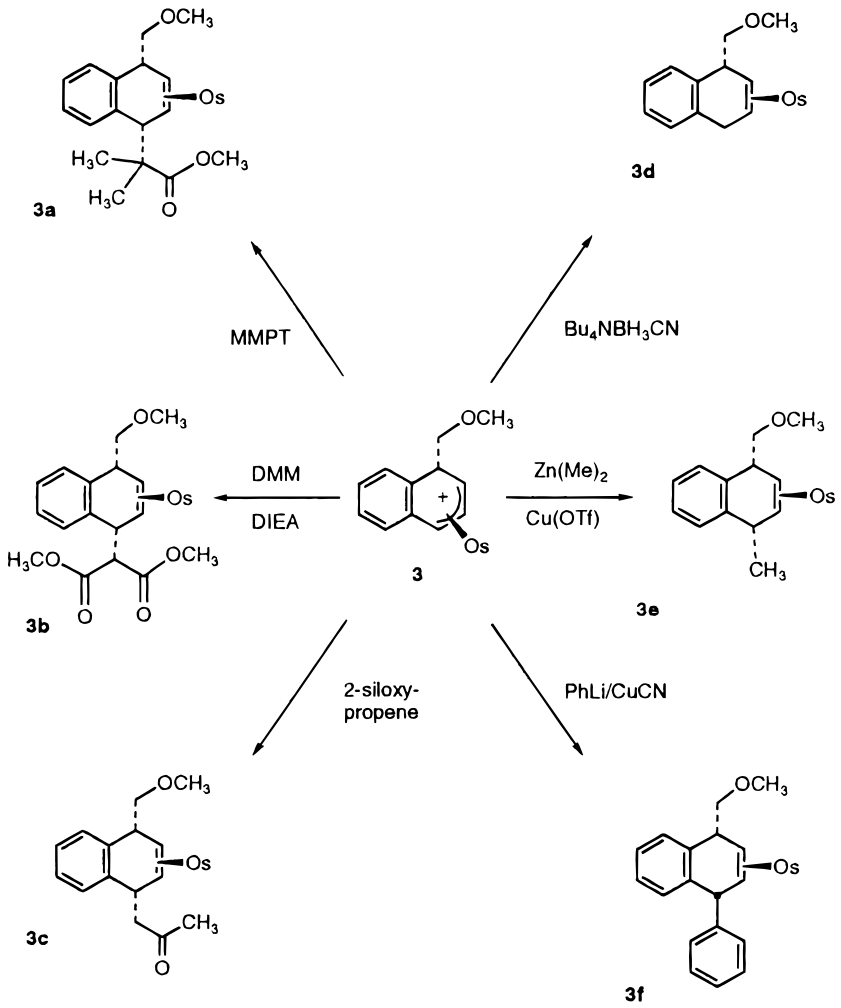



**Figure 3.** Nucleophilic addition reactions of the $\eta^3$-1-naphthalenium complex **3**.

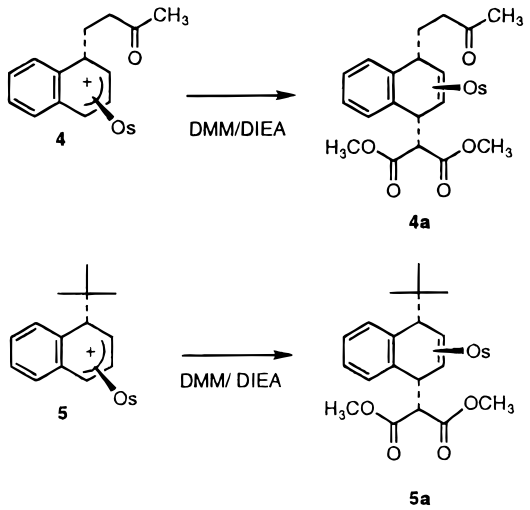
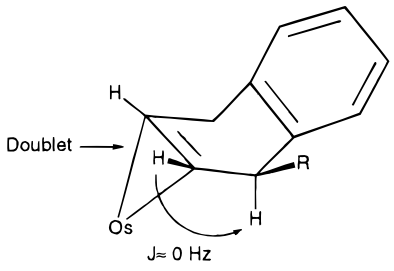



**Figure 4.** Nucleophilic addition reactions of the $\eta^3$-1-naphthalenium complexes **4** and **5**.

This protocol reduced the overall yield of the organic ligand (**5a′**) to 25% as a result of the low efficiency of the precipitation process.

The regiochemistry of the addition reaction was confirmed by comparison of the two vinyl protons in the organic products with values reported in the literature. The olefinic protons of 1,4-dihydronaphthalenes have chemical shifts that typically differ by less that 0.2 ppm in the $^1$H NMR spectrum and are rarely >6.1−6.2 ppm.[9−11] This is consistent with the observations for our reported compounds. For 1,2-dihydronaphthalenes the α proton is shifted to considerably lower field, usually >6.5 ppm.[3,12]

The stereochemistry of the reported 1,4-dihydronaphthalenes was confirmed by analysis of $^1$H NMR coupling data for the isolated complexes and their organic ligands. In every case examined, the coordinated olefinic protons are doublets. The lack of additional splitting indicates that the incoming

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substituents add to the ring face opposite to that of metal coordination, thereby creating dihedral angles of approximately 90° for H1−C1−C2−H2 and for H3−C3−C4−H4, consistent with a coupling constant close to 0 Hz.

The entire synthetic sequence outlined above, including the complexation of naphthalene, may be performed outside the glovebox without the aid of specialized glassware. We employed freshly activated magnesium stored under nitrogen, but otherwise, no special precautions were taken to purify or degas reagents. After complexation, the $\eta^2$-naphthalene complex was isolated then used immediately. As an example, the dihydronaphthalene **3a′** was prepared *on the bench* in overall 50% yield from naphthalene taking no precautions to dry solvents or glassware. This represents only a modest drop in yield compared to a 65% yield obtained using rigorously purified materials.

In a manner similar to naphthalene, anthracene and phenanthrene[13] form a stable complex with osmium(II) in which the metal binds across C1 and C2. Unlike the reactivity traditional observed for anthracene, chemistry takes place exclusively on the terminal ring.[8] The p$K_a$ for the 1-anthracenium complex of pentaammineosmium(II) (−8.0) is close to that of the 1-naphthalenium complex,[8] and our preliminary data indicate that addition of MVK occurs at C1 to generate a 1-anthracenium species analogous to **4**. Subsequent treatment with the nucleophile MMTP generates a 1,4-dihydroanthracene complex in good yield.

## Discussion

The 1,4-dihydronaphthalene skeleton is present in numerous natural products and is particularly prevalent in the lignanoid family.[1−3] The dearomatization methodology outlined herein provides a method for the rapid formation of *cis*-1,4-disubstituted naphthalenes from aromatic precursors. The diversity of substituents incorporated by this process is considerably broader than has been realized using the Birch process.[4] Consider for example the tricyclic lignanoid core **3f′** (Table 1), found in the natural products such as phyltetralin,[14] podophyllotoxin, or etoposide.[1] This material can be generated as a single regio- and stereoisomer from naphthalene, an acetal, and phenyllithium with an overall yield of 40%.

The pentaammineosmium(II) fragment functions by adding electron density into the ligand $\pi$ system through $\pi$ backbonding. As a consequence, electrophilic rather than nucleophilic addition occurs, contrary to what is usually observed for metal-mediated reactions with arenes[15] or naphthayloxazolines.[12,14,16] The site of the initial electrophilic addition is governed by the thermodynamic preference of the metal for binding across C1 and C2.[8,13] The observation that the nucleophilic addition occurs predominantly in a 1,4 manner is rationalized in Figure 5. In consideration of the two resonance structures that place a positive charge on a terminal carbon of the allyl system (I and III), only III allows further delocalization into the aromatic ring. Thus, the osmium is likely to be closer to C2 than to C4, and addition is kinetically favored at the latter carbon. Verification of this distortion in the bonding of the naphthalenium system using X-ray diffraction has been frustrated by difficulties in obtaining a suitable single crystal of the reactive 1-naphthalenium complexes, but similar distortions

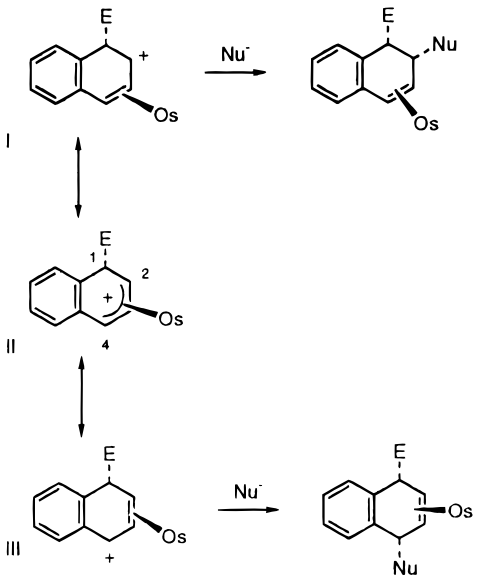


**Figure 5.** Resonance structure interpretation of 1,4 versus 1,2 addition.

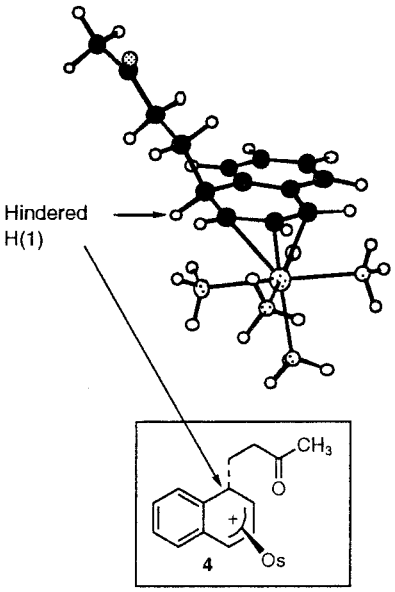


**Figure 6.** Molecular model showing kinetic stabilization against deprotonation at C1 of the $\eta^3$-naphthalenium complex (**4**).

in $\pi$-allyl complexes have been documented.[17,18] The observed cis stereochemistry is again a direct result of the metal, but in this case steric influences control the addition. The metal efffectively blocks one face of the naphthalene ligand, forcing attack of both electrophile and nucleophile to occur from the opposite face. The steric bulk of the metal also plays an important role in protecting the acidic proton at C1 of the 1-naphthalenium complexes (Figure 6). Correspondingly, although the p$K_a$ of the C1 proton rivals that of strong mineral acids, clean 1,4-addition is possible even with nucleophiles as basic as malonate anions.

## Conclusion

A new methodology for synthesizing *cis*-1,4-dihydronaphthalenes in good yields directly from naphthalene has been developed. This dearomatization procedure takes advantage of

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the electron-donating properties of pentaammineosmium(II) to promote electrophilic addition to C1 and to stabilize the 1-naphthalenium products such that a carbon-based nucleophile may be added. This process does not require use of any specialized glassware.

## Experimental Details

**General Procedure.** $^1$H and $^{13}$C NMR spectra were recorded on a General Electric GN-300 spectrometer unless otherwise noted. Chemical shifts are reported in parts per million relative to TMS ($\delta$ $CD_3CN$ = 1.93, acetone-$d_6$ = 2.04, $CDCl_3$ = 7.26, $CD_3OD$ = 3.30). 2D-NMR experiments (DEPT, NOE) were recorded on a General Electric GN-300 spectrometer as well. $^{13}$C multiplicities are supported by DEPT data. Electrochemical experiments were performed under nitrogen using a PAR model 362 potentiostat driven by a PAR model 175 universal programmer. Cyclic voltammograms were recorded (Kipp & Zonen BD90 XY recorder) in a standard three-electrode cell, from +1.7 to −1.7 V with a glassy carbon electrode. All potentials are reported vs NHE and, unless otherwise noted, were determined in acetonitrile (about 0.5 M TBAH) at 100 mV/s using cobaltocene ($E_{1/2}$= −0.78 V) in situ as a calibration standard. The peak-to-peak separation ($E_{p,a} - E_{p,c}$) was between 80 and 100 mV for all reversible couples unless otherwise noted. Some of this work was carried out under a nitrogen atmosphere in a Vacuum Atmospheres Co. glovebox.

**Solvents.** Acetonitrile-$d_3$ (Cambridge Isotope Labs) was refluxed over $CaH_2$ and distilled under argon. Acetone-$d_6$ (Cambridge Isotope Labs) was used as received except that it was deoxygenated prior to use. Methanol-$d_4$ (Cambridge Isotope Labs) was received in sealed ampules and used without any further purification, as was chloroform-*d* (Cambridge Isotope Labs).

**Reagents.** The precursor, $[Os(NH_3)_5OTf](OTf)_2$, was synthesized as earlier described.[8] Dimethoxymethane was dried over sodium and distilled under argon, methyl vinyl ketone was distilled under vacuum, and *tert*-butyl alcohol was dried over $CaH_2$ then distilled under argon. All other reagents were used as received. Both the complexes **1** and **2** were previously reported.[8]

**$[Os(NH_3)_5(2,3,4\text{-}\eta^3\text{-}1\text{-methoxymethyl-}1H\text{-naphthalenium})](OTf)_3$ (3).** Complex **1** (929 mg, 1.33 mmol) was dissolved in a solution of dimethoxymethane (268 mg, 3.53 mmol) in 2.50 g of $CH_3CN$, which was then treated with a solution of HOTf (416 mg, 2.78 mmol) in 2.50 g of $CH_3CN$. After 1 h, the solution was precipitated into ether and filtered through a fine frit to yield **3**, 1.04 g (1.16 mmol, 88%). $^1$H NMR (300 MHz, $CD_3CN$): $\delta$ 7.58 (d, $J$ = 6.6 Hz, 1H), 7.35 (m, 3H), 6.41 (dd, $J$ = 6.0, 2.1 Hz, 1H), 6.13 (m, 1H), 5.52 (t, $J$ = 6.3 Hz, 1H), 5.29 (br s, 3H), 4.08−3.98 (m, 2H), 3.89 (br s, 12H), 3.30 (s, 3H), 2.31 (m,1H). $^{13}$C NMR (75 MHz, $CD_3CN$): $\delta$ 133.2 (C), 132.7 (C), 132.3 (CH), 131.4 (CH), 130.6 (CH), 129.2 (CH), 86.3 (CH), 82.4 (CH), 76.4 (CH), 73.8 ($CH_2$), 59.3 ($CH_3$), 41.7 (CH). Anal. Calcd for $C_{15}H_{28}N_5O_{10}S_3F_9Os$: C, 20.11; H, 3.21; N, 7.82. Found: C, 19.77; H, 3.37; N, 8.03.

**$[Os(NH_3)_5(2,3,4\text{-}\eta^3\text{-}\{1\text{-}(3'\text{-oxobutyl})\text{-}1H\text{-naphthalenium}\})](OTf)_3$ (4).** To a stirring solution of **1** (535 mg, 0.76 mmol) dissolved in 3.52 g of $CH_3CN$ was added dropwise a solution of MVK (70 mg, 1.00 mmol) in 530 mg of $CH_3CN$, followed by HOTf (126 mg, 0.84 mmol) in 500 mg of $CH_3CN$. The solution was stirred rapidly for 15 min, and then, to ensure completion, a solution of MVK (39 mg, 0.56 mmol) in 500 mg of $CH_3CN$ was added, followed by a solution of HOTf (31 mg, 0.21 mmol) in 500 mg of $CH_3CN$. Stirring was continued for an additional 15 min, and the product was precipitated in diethyl ether to yield **4** (633 mg, 0.69 mmol, 90%). $^1$H NMR (300 MHz, $CD_3CN$): $\delta$ 7.57 (d, $J$ = 6.3 Hz, 1H), 7.35 (m, 3H), 6.42 (dd, $J$ = 5.7, 1.8 Hz, 1H), 6.04 (m, 1H), 5.50 (t, $J$ = 6.6 Hz, 1H), 5.27 (br, s, 3H), 3.85 (br, s, 12H), 2.65−2.20 (m, 5H), 2.05 (s, 3H). $^{13}$C NMR (75 MHz, acetone-$d_6$): $\delta$ 207.3 (C), 135.1 (C), 132.7 (C), 131.7 (CH), 130.7 (CH), 129.8 (CH), 128.2 (CH), 84.6 (CH), 83.4 (CH), 75.6 (CH), 39.0 (CH), 38.9 ($CH_2$), 29.5 ($CH_3$), 28.5 ($CH_2$). Anal. Calcd for $C_{17}H_{30}N_5O_{10}S_3F_9Os$: C, 22.15; H, 3.28; N, 7.60. Found: C, 21.76; H, 3.26; N, 7.75.

**$[Os(NH_3)_5(2,3,4\text{-}\eta^3\text{-}\{1\text{-}tert\text{-butyl-}1H\text{-naphthalenium}\})](OTf)_3$ (5).** Complex **1** (358 mg, 0.51 mmol) was dissolved in a solution of *tert*-butyl alcohol (297 mg, 4.02 mmol) in 1.91 g of $CH_3CN$, which was then treated with a solution of triflic anhydride (941 mg, 3.35 mmol) in 1.90 g of $CH_3CN$. After 2 h, the solution was precipitated into ether and filtered to yield **5**, 347 mg (0.38 mmol, 75%). $^1$H NMR (300 MHz, $CD_3CN$): $\delta$ 7.54 (d, $J$ = 7.5 Hz, 1H), 7.38 (td, $J$ = 7.2, 1.5 Hz, 1H), 7.28 (dd, $J$ = 7.5, 1.2 Hz, 1H), 7.38 (td, $J$ = 7.5, 1.5 Hz, 1H), 6.42 (dd, $J$ = 6.0, 2.4 Hz, 1H), 6.20 (m, 1H), 5.77 (t, $J$ = 6.1 Hz, 1H), 5.28 (br s, 3H), 3.82 (br s, 12H), 2.25 (d, $J$ = 3.0 Hz, 1H), 1.08 (s, 9H). $^{13}$C NMR (75 MHz, $CD_3CN$): $\delta$ 133.7 (C), 133.0 (C), 132.6 (CH), 131.9 (CH), 131.7 (CH), 130.1 (CH), 88.0 (CH), 86.2 (CH), 77.1 (CH), 50.6 (CH), 35.0 (C), 28.8 ($CH_3$).

**$[Os(NH_3)_5(2,3\text{-}\eta^2\text{-}1,4\text{-dihydronaphthalene})](OTf)_2$ (2a).** Complex **1** (90 mg, 0.13 mmol) was dissolved in a solution of HOTf (397 mg, 2.64 mmol) in 1.02 g of $CH_3CN$ and stirred. The stirring solution was then treated with a solution of triethylsilane (404 mg, 3.49 mmol) in 950 mg of $CH_3CN$. The stirring was continued for 0.5 h, and the solution was precipitated into ether and filtered to yield **2a** (85 mg, 0.12 mmol, 93%). $^1$H NMR (300 MHz, $CD_3CN$): $\delta$ 7.08 (m, 4H), 4.18 (d, $J$ = 19.8 Hz, 2H), 3.91 (br, s, 3H), 3.69 (s, 2H), 2.93 (d, $J$ = 19.8 Hz), 2.75 (br, s, 12H).

**1,4-Dihydronaphthalene (2a′).** Complex **2a** was dissolved in a solution of diisopropylethylamine (DIEA) (45 mg, 0.35 mmol) in 3.0 g of $CH_3CN$. To this solution was added AgOTf (214 mg, 0.83 mmol) and vigorous stirring was started. At the end of 0.5 h, the solution was transferred to a pressure tube and heated at 80 °C for another 0.5 h. The solution was cooled and added to stirring ether, followed by filtration of all precipitates. The ether was removed, and column chromatography of the product using hexanes yielded 41 mg of **2a′** (0.32 mmol, 60%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.14 (br, s, 4H), 6.01 (br, s, 2H), 3.41 (br, s, 4H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 135.3 (C), 129.7 (CH), 126.6 (CH), 125.6 (CH), 30.9 ($CH_2$).

**$[Os(NH_3)_5\{2,3\text{-}\eta^2\text{-}(1\text{-}(2'\text{-}(2'\text{-carbomethoxy})\text{propyl})\text{-}1,4\text{-dihydronaphthalene})\}](OTf)_2$ (2b).** $^1$H NMR (300 MHz, $CD_3OD$): $\delta$ 7.13 (m, 4H), 4.30 (dd, $J$ = 18.9, 3.6 Hz, 1H), 4.29 (br s, 3H), 3.76 (s, 3H), 3.65 (dd, $J$ = 9.0, 3.6 Hz, 1H), 3.43 (s, 1H), 3.36 (d, $J$ = 9.0 Hz, 1H), 3.02 (br, s, 12H), 2.91 (d, $J$ = 18.9, 1H), 1.26 (s, 3H), 1.24 (s, 3H). $^{13}$C NMR (75 MHz, acetone-$d_6$): $\delta$ 178.4 (C), 137.8 (C), 136.2 (C), 131.6 (CH), 129.5 (CH), 127.5 (CH), 126.0 (CH), 52.3 (C), 51.8 ($CH_3$), 50.8 (CH), 49.1 (CH), 48.9 (CH), 32.3 ($CH_2$), 25.2 ($CH_3$), 20.3 ($CH_3$). Cyclic voltammetry: $E_{p,a}$ = 0.68 V.

**1-(2′-(2′-Carbomethoxy)propyl)-1,4-dihydronaphthalene (2b′).** Complex **1** (402 mg, 0.57 mmol) was dissolved in a solution of HOTf (430 mg, 2.86 mmol) in 1.09 g of $CH_3CN$ and cooled to −40 °C, then added to another −40 °C solution of methyl trimethylsilyl dimethylketene acetal (714 mg, 4.10 mmol) in 1.10 g of $CH_3CN$ and allowed to react for an additional 10 min at −40 °C. The solution was warmed to room temperature and added to 5 mL of $H_2O$ that contained HOTf (108 mg, 0.72 mmol). Diethyl ether (5 mL) was added, and the solution was stirred rapidly. To this rapidly stirring solution was added AgOTf (319 mg, 1.24 mmol), and stirring was continued for 0.5 h, after which time the entire solution was transferred to a pressure tube and heated at 80 °C for another 0.5 h. After cooling, the solution was extracted with ether and column chromatography on silica gel (200 mL of 5% ether/petroleum ether, 100 mL of 10% ether/petroleum ether, then 20% ether/petroleum ether until completion) yielded 102 mg of **2b′**, (0.45 mmol, 77%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.20−7.07 (m, 4H), 6.18 (dd, $J$ = 9.9, 2.4 Hz, 1H), 5.95 (m,1H), 3.86 (m, 1H), 3.73 (s, 3H), 3.44 (m, 1H), 3.26 (dd, $J$ = 16.2, 2.1 Hz, 1H), 1.08 (s, 3H), 1.07 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 177.8 (C), 136.5 (C), 135.1 (C), 128.9 (CH), 128.4 (CH), 128.1 (CH), 126.7 (CH), 126.1 (CH), 125.3 (CH), 51.7 (CH), 50.0 (C), 47.1 (CH), 31.1 ($CH_2$), 22.1 ($CH_3$), 21.4 ($CH_3$).

**$[Os(NH_3)_5\{2,3\text{-}\eta^2\text{-}(1\text{-(methoxymethyl)-4-}(2'\text{-}(2'\text{-carbomethoxy})\text{-propyl})\text{-}1,4\text{-dihydronaphthalene})\}](OTf)_2$ (3a).** $^1$H NMR (300 MHz, acetone-$d_6$): $\delta$ 7.24 (d, $J$ = 6.9 Hz, 1H), 7.20−7.11 (m, 3H), 4.57 (br s, 3H), 3.95 (d, $J$ = 9.0 Hz, 1H), 3.82 (d, $J$ = 6.9 Hz, 1H), 3.71 (s, 3H), 3.69 (m, 1H), 3.49 (d, $J$ = 9.0 Hz, 1H), 3.39 (s, 3H), 3.35 (br s, 12H), 3.26−3.15 (m, 2H), 1.29 (s, 3H), 1.17 (s, 3H). $^{13}$C NMR (75 MHz, acetone-$d_6$): $\delta$ 179.5 (C), 138.7 (C), 135.7 (C), 132.4 (CH), 131.6 (CH), 128.0 (CH), 126.7 (CH), 81.9 (CH2), 58.9 (CH3), 52.6 (CH3),

51.7 (CH3), 51.0 (C), 50.7(CH), 48.9 (CH), 43.3 (CH), 27.3 (CH3), 21.7 (CH3). Cyclic voltammetry: $E_{p,a} = 0.70$ V.

**1-(Methoxymethyl)-4-(2′-(2′-carbomethoxy)propyl)-1,4-dihydronaphthalene (3a′).** The procedure for **3** was followed starting with 233 mg (0.33 mmol) of complex **1**, but the product was not precipitated at the end of 1 h. The solution of **3** was instead transferred to a −40 °C bath where it was cooled for 25 min, then treated with a −40 °C solution of methyl trimethylsilyl dimethylketene acetal (292 mg, 1.68 mmol) in 730 mg of $CH_3CN$. This new solution was allowed to react for an additional 10 min at −40 °C, then added to 5 mL of $H_2O$ at room temperature. Diethyl ether (5 mL) was then added, and the solution was started stirring rapidly. To this stirring solution was added AgOTf (211 mg, 0.82 mmol), and vigorous stirring was continued for 0.5 h, after which the entire solution was transferred to a pressure tube and heated at 80 °C for another 0.5 h. After cooling, the solution was extracted with ether and column chromatography on silica gel (200 mL of 5% ether/petroleum ether, 100 mL of 10% ether/petroleum ether, then 20% ether/petroleum ether until completion) yielded 59 mg of **3a′** (0.22 mmol, 65%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.29 (dd, $J$ = 7.2, 1.5 Hz, 1H), 7.23−7.1 (m, 2H), 7.04 (d, $J$ = 7.8 Hz, 1H), 6.14 (dd, $J$ = 10.35, 4.5 Hz, 1H), 5.85 (dd, $J$ = 10.35, 4.5 Hz, 1H), 3.95 (m, 1H), 3.75 (s, 3H), 3.69 (m, 3H), 3.41 (s, 3H), 1.11 (s, 3H), 1.07 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 178.1 (C), 136.6 (C), 134.7 (C), 129.3 (CH), 129.1 (CH), 128.7 (CH), 126.3 (CH), 126.1 (CH), 125.8 (CH), 78.6 ($CH_2$), 58.9 ($CH_3$), 51.8 ($CH_3$), 47.2 (C), 46.3 (CH), 40.7 (CH), 23.1 ($CH_3$), 22.6 ($CH_3$). Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 73.98; H, 8.30.

**Benchtop Procedure**. The procedure was started with 1.06 g of $[Os(NH_3)_5(OTf)](OTf)_2$ dissolved in 3.3 g of degassed DMAc in a 10-mL round-bottom flask. It is important to eliminate oxygen from the solvent before addition of the ligand and $Mg^0$. Next 1.96 g of naphthalene was added and stirring was commenced before the first 1.5 g of $Mg^0$ was added. If the magnesium is not stored under nitrogen, the magnesium should be activated ($I_2$) prior to use and used immediately. After 0.5 h, another 1.5 g of $Mg^0$ was added to ensure completion of the complexation, and stirring was continued for an additional 0.5 h. At the end of this 1 h, the solution was filtered through a 125-mL medium frit into a stirring solution of $CH_2Cl_2$, and the resulting precipitate was filtered and washed with more $CH_2Cl_2$ followed by ether to yield 880 mg (1.25 mmol) of naphthalene complex (85%). The complex was immediately placed into a 25-mL round-bottom flask under an atmosphere of argon, dissolved in a solution of dimethoxymethane (257 mg, 3.38 mmol) in 2.12 g of $CH_3CN$, and treated with a solution of HOTf (406 mg, 2.71 mmol) in 2.1 g of $CH_3CN$. At the end of 1 h, the flask was placed into a −40 °C bath where it was cooled for 25 min, then treated with a −40 °C solution of methyl trimethylsilyl dimethylketene acetal (1.10 g, 6.31 mmol) in 540 mg of $CH_3CN$. This new solution was allowed to react for an additional 10 min at −40 °C, then added to 5 mL of $H_2O$ containing HOTf (280 mg, 1.87 mmol) at room temperature. Diethyl ether (5 mL) was then added, and the solution was started stirring rapidly. To this stirring solution was added AgOTf (651 mg, 2.53 mmol), and vigorous stirring was continued for 0.5 h, after which the entire solution was transferred to a pressure tube and heated at 80 °C for another 0.5 h. After cooling, the solution was extracted with ether and column chromatography on silica gel (200 mL of 5% ether/petroleum ether, 100 mL of 10% ether/petroleum ether, then 20% ether/petroleum ether until completion) yielded 171 mg of **3a′** (0.63 mmol, 50%).

**$[Os(NH_3)_5\{2,3\text{-}\eta^2\text{-}(1\text{-(methoxymethyl)-4-(2′-dimethyl malonate)-1,4-dihydronaphthalene)}\}](OTf)_2$ (3b).** $^1$H NMR (300 MHz, acetone-$d_6$): $\delta$ 7.18−7.08 (m, 3H), 6.98 (d, $J$ = 6.9 Hz, 1H), 4.59 (br s, 3H), 4.10 (d, $J$ = 9.6 Hz, 1H), 3.78 (d, $J$ = 9.6 Hz, 1H), 3.73 (s, 3H), 3.47 (s, 3H), 3.36 (br s, 12H), 3.31 (s, 3H), 3.29−3.22 (m, 4H), 2.86 (d, $J$ = 5.7 Hz, 1H). $^{13}$C NMR (75 MHz, acetone-$d_6$): $\delta$ 179.5 (C), 138.7 (C), 135.8 (C), 132.4 (CH), 131.6 (CH), 127.9 CH), 126.7 (CH), 81.9 ($CH_2$), 58.9 ($CH_3$), 52.6 ($CH_3$), 51.7 (CH), 51.0 (C), 50.7 (CH), 48.9 (CH), 43.3 (CH), 27.3 ($CH_3$), 21.7 ($CH_3$). Cyclic voltammetry: $E_{p,a}$ = 0.73 V.

**1-(Methoxymethyl)-4-(2′-dimethyl malonate)-1,4-dihydronaphthalene (3b′).** The procedure for **3** was followed starting with 171 mg (0.24 mmol) of complex **1** but was not precipitated at the end of 1 h. The solution of **3** was instead transferred to a −40 °C bath where it was cooled for 25 min, then treated with a −40 °C solution of dimethyl malonate (175 mg, 1.33 mmol) and DIEA (64 mg, 0.50 mmol) in 440 mg of $CH_3CN$. This new solution was allowed to react for an additional 10 min at −40 °C, and then added to 5 mL of $H_2O$ at room temperature. Diethyl ether (5 mL) was then added, and the solution was started stirring rapidly. To this stirring solution was added HOTf (52 mg, 0.35 mmol) and AgOTf (148 mg, 0.57 mmol), and vigorous stirring was continued for 0.5 h, after which the entire solution was transferred to a pressure tube and heated at 80 °C for another 0.5 h. After cooling, the solution was extracted with ether, then back extracted with 10% NaOH. Column chromatography on silica gel (200 mL of 5% ether/petroleum ether, 100 mL of 10% ether/petroleum ether, then 20% ether/petroleum ether until completion) yielded 40 mg of **3b′** (0.13 mmol, 54%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.22 (m, 4H), 6.22 (m, 2H), 4.25−4.22 (m, 1H), 3.72 (s, 3H), 3.71−3.53 (m, 4H), 3.65 (s, 3H), 3.36 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 168.6 (C), 168.3 (C), 136.2 (C), 134.9 (C), 129.0 (CH), 128.5 (CH), 127.7 (CH), 127.0 (CH), 126.7 (CH), 126.2 (CH), 77.5 ($CH_2$), 59.3 ($CH_3$), 60.0 (CH), 52.6 ($CH_3$), 52.6 ($CH_3$), 41.1 (CH), 39.5 (CH). Anal. Calcd for $C_{17}H_{20}O_5$ : C, 67.09; H, 6.62. Found: C, 66.56; H, 6.84.

**$[Os(NH_3)_5\{2,3\text{-}\eta^2\text{-}(1\text{-(methoxymethyl)-4-(1′-propan-2′-one)-1,4-dihydronaphthalene)}\}](OTf)_2$ (3c).** $^1$H NMR (300 MHz, $CD_3CN$): $\delta$ 7.15−7.05 (m, 4H), 3.98 (br s, 3H), 3.71 (dd, $J$ = 9.0, 5.7 Hz, 1H), 3.63 (dd, $J$ = 9.0, 5.4 Hz, 1H), 3.57 (d, $J$ = 9.0 Hz, 1H), 3.49 (d, $J$ = 9.0 Hz, 1H), 3.31 (s, 3H), 3.24−2.97 (m, 4H), 2.81 (br s, 12H), 2.15 (s, 3H). $^{13}$C NMR (75 MHz, $CD_3CN$): $\delta$ 209.9 (C), 140.0 (C), 137.6 (C), 130.9 (CH), 129.8 (CH), 128.2 (CH), 127.4 (CH), 82.7 ($CH_2$), 59.2 ($CH_3$), 56.9 ($CH_2$), 53.6 (CH), 50.9 (CH), 42.9 (CH), 37.6 (CH), 30.9 ($CH_3$). Cyclic voltammetry: $E_{p,a}$ = 0.66 V.

**1-(Methoxymethyl)-4-(1′-propan-2′-one)-1,4-dihydronaphthalene (3c′).** The procedure for **3** was followed starting with 364 mg (0.52 mmol) of complex **1** but was not precipitated at the end of 1 h. The solution of **3** was instead transferred to a −40 °C bath where it was cooled for 25 min and then treated with a −40 °C solutions of di-*tert*-butylpyridine (209 mg, 1.09 mmol) in 820 mg of $CH_3CN$ and siloxypropene (366 mg, 2.81 mmol). This new solution was allowed to react for an additional 1 h at −40 °C, then added to 5 mL of $H_2O$ at room temperature. Diethyl ether (5 mL) was then added, and the solution was started stirring rapidly. To this stirring solution was added AgOTf (350 mg, 1.36 mmol), and vigorous stirring was continued for 0.5 h, after which the entire solution was transferred to a pressure tube and heated at 80 °C for another 0.5 h. After cooling, the solution was extracted with ether and column chromatography on silica gel (petroleum ether until the di-*tert*-butylpyridine was gone, then 200 mL of 5% ether/petroleum ether, 100 mL of 10% ether/petroleum ether, and 20% ether/petroleum ether until completion) yielded 83 mg of **3c′** (0.36 mmol, 69%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.20 (m, 4H), 6.09 (dd, $J$ = 10.2, 4.8, 1H), 5.98 (dd, $J$ = 10.2, 4.2, 1H), 3.96 (m, 1H), 3.59 (m, 1H), 3.56 (dd, $J$ = 8.4, 5.4, 1H), 3.46 (dd, $J$ = 8.4, 6.6, 1H), 3.35 (s, 3H), 2.83 (dd, $J$ = 16.95, 5.1, 1H), 2.69 (dd, $J$ = 16.95, 9.0, 1H), 2.13 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 207.1 (C), 138.4 (C), 135.7 (C), 129.8 (CH), 128.6 (CH), 127.8 (CH), 127.2 (CH), 126.6 (CH), 126.1 (CH), 78.9 (CH2), 59.0 ($CH_3$), 54.3 ($CH_2$), 40.6 (CH), 35.3 (CH), 30.7 ($CH_3$). Anal.Calcd for $C_{15}H_{18}O_2$ : C, 78.23; H, 7.88. Found: C, 77.88; H, 8.29.

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**Supporting Information Available:** Text giving experimental procedures and characterizations for all compounds described in this account (7 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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